Kinetics of the Reaction between Hexacyanoferrate(III) and Thiosulphate Ions. The Initial Reaction

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The kinetics of the reaction between hexacyanoferrate(III) and thiosulphate in aqueous solution have been investigated spectrophotometrically. The rate equation contains several terms. Results on the first few percent of reaction only are analysed here. The total initial rate consists of an uncatalysed part, viz. $-d[Fe(CN)_6^{3-}]/dt = 38[H^+][S_2O_3^{2-}]^2$ mol l^{-1} min^{-1} at 298° K together with components caused by catalysis by acetate and by cations. The mechanistic reasons for this are investigated and the uncatalysed path is shown to correspond in rate to the decomposition of thiosulphate.

Introduction

The reaction between hexacyanoferrate(III) and thiosulphate ions, in the absence of deliberately added catalysts, has been the subject of two earlier publications[1,2]. These kinetic data were consistent with a rate law of first order with respect to each of the two reactants. Catalysis by the product, tetrathionate, was found to be important in the later stages of reaction. Batstone[3] studied the reaction in an attempt to explain certain anomalies in the Harcourt–Esson[4] method for following the oxidation of iodide by hexacyanoferrate(III) and the results were in general agreement with those of the earlier workers. Spiro and Barreira[5], on the other hand, resolved the kinetic data into a rate law comprised of the sum of three terms, one of which described the initial rate and the other two explained tetrathionate catalysis. The terms were complex and included fractional order dependences.

Owing to the variation in reported results a re-investigation of the reaction is required. It is necessary to examine the isolated rate law corresponding to the "primary" and tetrathionate catalysed processes as a function of reaction variables. The former will be considered in this paper by measurements on initial rates, where the complications arising from the presence

of products are absent. A spectrophotometric technique, as adopted by Spiro and Barreira, is preferred to the iodometric titration used by others.

Experimental

Reactants were "Analar" reagents. Stock thiosulphate solutions were made slightly alkaline and were renewed frequently. Potassium hexacyanoferrate(III) solutions were prepared immediately before use. Thermostatted, buffered solutions were mixed and an aliquot was rapidly transferred to a glass cell in the thermostatted cell block of an SP800 spectrophotometer, operating in the fixed wavelength mode. Absorbance was recorded at 23,810 cm^{-1} at a scale expansion of 20, and initial rates were determined from the nearly linear plots of absorbance as a function of time. At 23,810 cm^{-1}, all dissolved species present except the hexacyanoferrates are transparent. The extinction coefficient for $Fe(CN)_6^{4-}$ is about 2% of that for $Fe(CN)_6^{3-}$; hence over the first 5% of reaction the absorbance is directly proportional to $[Fe(CN)_6^{3-}]$ within experimental error.

Results

Preliminary experiments over the greater part of the reaction showed that the rate is uninfluenced by the extent of surface or illumination or by the presence of oxygen in the headspace above the reaction mixture. The effect of Na$_2$EDTA on the first 5% of reaction was two-fold. An appreciable reduction in rate was accompanied by a much more consistent and linear plot. The addition of 10^{-4} mol l^{-1} of Na$_2$EDTA to reaction mixtures containing 10^{-2} mol l^{-1} S$_2$O$_3^{2-}$ and 10^{-3} mol l^{-1} Fe(CN)$_6^{3-}$ at 298° K and pH = 3.86 caused the initial rate to drop to about half its value in the absence of EDTA. No further effect on rate accompanied a 10-fold increase in [EDTA]. All runs reported here therefore contained 5 × 10^{-4} mol l^{-1} Na$_2$EDTA to eliminate catalysis by traces of multivalent cations. This addition of EDTA

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means that the present results probably refer to a different system from that employed by earlier workers.

At constant ionic strength and keeping $[Na^+]$ and $[K^+]$ constant, with $1.6–14.0 \times 10^{-4}$ mol l^{-1} $K_3Fe(CN)_6$; $0.65–4.57 \times 10^{-5}$ mol l^{-1} H^+ and $1–3 \times 10^{-2}$ mol l^{-1} $S_2O_3^{2-}$ the initial rate of reaction was found to be independent of the concentration of hexacyanoferrate(III) ion; of first order with respect to hydrogen ions (supplied by an acetic acid/acetate ion buffer at constant acetate ion concentration) and of second order with respect to thiosulphate ion. For experiments designed to study the dependence of rate on $[S_2O_3^{2-}]$ the concentration of sodium ions and of divalent anion was maintained by the addition of sodium sulphate. A selection of these results obtained at $298.1°K$ is given in Table I, and may be summarised as

$$-d[Fe(CN)_6^{3-}]/dt = k_3[H^+][S_2O_3^{2-}]^2$$

According to the Brønsted formulation, the rate constant, k_3, for such a reaction should be independent of ionic strength, I. The effect of I and of added salts was investigated by measuring the initial rate in the presence of added sodium or potassium nitrate such that, in any mixture, only one cation was present in significant amount. The constant k_3 decreased from a value of 71 mol^{-2} l^2 min^{-1} in the absence of added sodium nitrate (but with 0.054 mol l^{-1} Na^+ and 0.003 mol l^{-1} K^+) to 48 mol^{-2} l^2 min^{-1} with 0.480 mol l^{-1} $NaNO_3$. When K^+ was the only cation present, k_3 was unaffected by the addition of the salt, a value of 82 mol^{-2} l^2 min^{-1} being obtained with 0–0.390 mol l^{-1} KNO_3. For these calculations of k_3, $[H^+]$ is taken as $\log^{-1} \{0.505 F(I)–pH\}$ where $F(I) = \{\sqrt{I}/(1 + \sqrt{I})–0.2 I\}$ and $[S_2O_3^{2-}]$ is the concentration of thiosulphate ion as added. At first sight the behaviour of k_3 appears to be consistent with the rate equation in the presence of K^+, but not in the presence of Na^+. How-

ever, since protonation of $S_2O_3^{2-}$ is expected to be important in this reaction, addition of cation, by leading to the formation of ion pairs such as $NaS_2O_3^-$ and $KS_2O_3^-$, will reduce the concentration of $HS_2O_3^-$ and hence lower the rate. If cation catalysis of the $Fe(CN)_6^{3-}/S_2O_3^{2-}$ reaction is also possible, then different catalytic efficiencies of Na^+ and K^+ could account for the apparent, and possibly fortuitous, independence of rate on $[K^+]$. A more complete analysis therefore follows considering the concentrations of possible ion pairs in the reaction mixture.

The anions added were $EDTA^{4-}$, $Fe(CN)_6^{3-}$, $S_2O_3^{2-}$, NO_3^- and CH_3COO^-. For protonation equilibria at pH 4 and $298°K$, $EDTA^{4-}$ will exist mainly as H_2EDTA^{2-} (pK values for second and third dissociations are 2.67 and 6.16 respectively[6]), hexacyanoferrate(III) is not protonated (the third dissociation constant of $H_3Fe(CN)_6$ is too large to obtain evidence of complex formation[6]) and thiosulphate exists mainly as $S_2O_3^{2-}$ in about 100:1 molar excess[6] over $HS_2O_3^-$. The dissociation equilibrium constants for ion pairs formed between Na^+ or K^+ and anions are approximately dependent only on the nature of the cation and the charge type of the anion if no specialised interaction occurs. Thus, for the equilibrium:

$$ML^- \rightleftharpoons M^+ + L^{2-}$$

for $M^+ = Na^+$ and K^+, $K_o = 0.21$ and 0.11 mol l^{-1} respectively at $298°K$ and $I \to 0$, where L^{2-} is a divalent anion[6]. Few data are available regarding the stability of complexes ML^{2-}; the dissociation constant for $KFe(CN)_6^{2-}$ is reported as 0.8 mol l^{-1} at $298°K$ and $I \to 0$[6]. Sodium and potassium ions do not, in general, form stable ion pairs with univalent anions.

For the calculation of ion pair concentrations, the divalent anion concentration was taken as $[S_2O_3^{2-}] + [H_2EDTA^{2-}]$. The concentration of $Fe(CN)_6^{3-}$ amounts to some 10% of this and its stability constant

TABLE I. Selection of experiments carried out to investigate the effect of reactant concentration on rate.

$[S_2O_3^{2-}]$ mol l^{-1}	$[Fe(CN)_6^{3-}]$ mol l^{-1}	$[Na^+]$ mol l^{-1}	$[K^+]$ mol l^{-1}	$[CH_3COO^-]$ mol l^{-1}	pH	I	Initial Rate[a]
0.0200	0.000156	0.041	0.200	0.200	5.17	0.26	6.67
0.0200	0.000467	0.041	0.201	0.200	5.17	0.26	6.49
0.0200	0.000109	0.041	0.203	0.200	5.17	0.27	6.69
0.0200	0.00140	0.041	0.204	0.200	5.17	0.27	6.49
0.0200	0.00100	0.041	0.036	0.033	5.19	0.10	3.30
0.0200	0.00100	0.041	0.036	0.033	4.75	0.10	8.1
0.0200	0.00100	0.041	0.036	0.033	4.54	0.10	12.5
0.0200	0.00100	0.041	0.036	0.033	4.34	0.10	20.4
0.0100	0.00100	0.067	0.036	0.033	4.22	0.10	6.5
0.0166	0.00100	0.067	0.036	0.033	4.22	0.10	20.0
0.0200	0.00100	0.067	0.036	0.033	4.22	0.10	28.8
0.0233	0.00100	0.067	0.036	0.033	4.22	0.10	36.9

[a] $10^7 (-d[Fe(CN)_6^{3-}]/dt)$ mol l^{-1} min^{-1}.
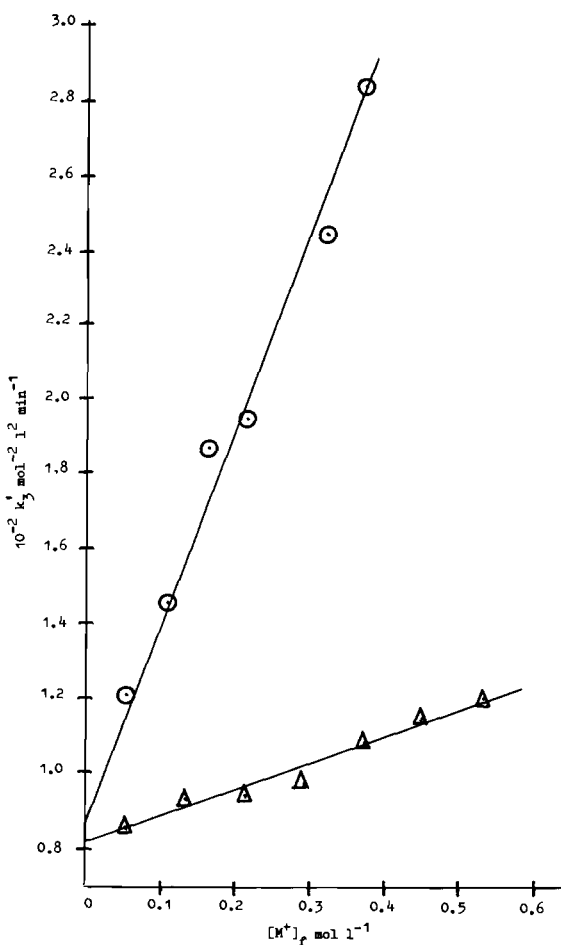
Figure 1. Dependence of third order rate constant on cation concentration. $\odot$, K^+; $\triangle$, Na^+.

with K^+ is not remote from that expected for KL^-. Hence, to a good approximation $[Fe(CN)_6^{3-}]$ was included in $[L^{2-}]$. Equilibrium constants at any ionic strength were calculated from $K = K_o \log^{-1} \{2.02 F(I)\}$ where $F(I)$ is the function of ionic strength used above.

Thus, the concentrations of "free" thiosulphate and "free" M^+ were calculated together with improved values for I. The new values are denoted by the subscript "f" and rate constants k_3' are calculated according to the rate expression:

$$-d[Fe(CN)_6^{3-}]/dt = k_3' [H^+][S_2O_3^{2-}]_f^2$$

Figure 1 shows the dependence of k_3' on $[Na^+]_f$ and $[K^+]_f$. From this graph it follows that at $298°\,K$, when $[Na^+] = [K^+] = 0$, $k_3 = 85 \, mol^{-2} \, l^2 \, min^{-1}$ with $0.033 \, mol \, l^{-1}$ acetate ion, and that the reaction exhibits cation catalysis. The best rate equation fitting the catalysed part of the reaction is:

$$-d[Fe(CN)_6^{3-}]/dt = 10^{-3.03F(I)} \{3.2[Na^+]_f + 23.4[K^+]_f\}[H^+][S_2O_3^{2-}]_f$$

Table II shows the agreement of initial rates calculated from the sum of cation catalysed and uncatalysed reactions with experimentally measured rates. The first order dependence with respect to thiosulphate for the catalysed reaction is consistent with the findings of Spiro and Barreira[5] for initial rates measured in 2 $mol \, l^{-1}$ salt solution.

In separate experiments the rate constant at low $[Na^+]$ and $[K^+]$ was found to be dependent on the concentration of acetate ion where:

$$k_3' = 38 + 1400 \, [CH_3COO^-]$$

The consistency of this result over a sixfold concentration change is shown in Table III.

The solvent isotope effect was measured by preparing identical buffered reaction mixtures at low salt concentration in H_2O and in 95% D_2O. The reaction is faster in H_2O than in D_2O by a factor of 1.4.

At low cation concentration the apparent activation energy is $70.2 \, kJ \, mol^{-1}$; and in the presence of $0.356 \, mol \, l^{-1} \, KNO_3$ it is $74.8 \, kJ \, mol^{-1}$. These results refer to the temperature range 288 to $313°\,K$.

The effects of products on rate are important[1,2,3,5] in the later stages of reaction, but they are not significant in our initial rate studies. They will be considered in detail in a later publication.

Discussion

Initial Stages of the Uncatalysed Reaction

The initial rate of reaction is independent of the concentration of $Fe(CN)_6^{3-}$ and appears anomalous as a redox reaction involving thiosulphate, because the concentration of the oxidant normally appears in the rate expression[7]. The implication is that thiosulphate undergoes a spontaneous rate-determining change in the buffered medium which facilitates electron removal by hexacyanoferrate(III).

One spontaneous process known to occur to thiosulphate in aqueous solution is acid catalysed decomposition to sulphur, sulphite and polythionate. Dinegar *et al.*[8] studied the rate of formation of colloidal sulphur in acidified thiosulphate solutions and reported the rate of production of the element as

$$d[S]/dt = k[S_2O_3^{2-}]^{3/2}[H^+]^{1/2}$$

This corresponds to the very early stages of decomposition and was shown to be consistent with the consecutive reactions:
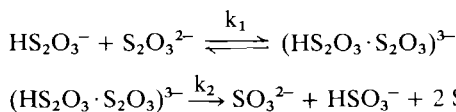
$$HS_2O_3^- + S_2O_3^{2-} \underset{}{\overset{k_1}{\rightleftharpoons}} (HS_2O_3 \cdot S_2O_3)^{3-}$$

$$(HS_2O_3 \cdot S_2O_3)^{3-} \xrightarrow{k_2} SO_3^{2-} + HSO_3^- + 2\,S$$

TABLE II. Comparison of data for uncatalysed and cation catalysed components of the initial rate with experimentally observed results.

[NaNO$_3$] mol l^{-1}	pH	I	Uncatalysed Rate[a]	Catalysed Rate[a]	Total Calc. Initial Rate[a]	Initial Rate (obs)[a]
0	4.15	0.07	6.23	0.36	6.59	6.30
0.080	4.16	0.15	5.49	0.58	6.07	6.03
0.160	4.14	0.23	5.24	0.77	6.01	5.80
0.240	4.10	0.31	5.24	0.99	6.23	5.99
0.320	4.01	0.39	5.87	1.38	7.25	7.52
0.400	4.06	0.47	4.75	1.36	6.11	6.45
0.480	3.98	0.55	5.16	1.80	6.96	7.30
[KNO$_3$] mol l^{-1}						
0	4.11	0.07	5.68	2.68	8.36	8.10
0.054	4.14	0.12	4.45	3.53	8.07	7.76
0.107	4.15	0.18	3.93	4.12	8.05	8.65
0.160	4.12	0.23	3.77	4.93	8.70	8.63
0.267	4.09	0.34	3.29	6.19	9.48	9.44
0.320	4.09	0.39	2.98	6.58	9.56	10.00

[a] Experiments carried out at 298.1° K with 0.0100 mol l^{-1} Na$_2$S$_2$O$_3$, 0.00100 mol l^{-1} K$_3$Fe(CN)$_6$ and 0.033 mol l^{-1} CH$_3$COO$^-$. All rates 10^7 (−d[Fe(CN)$_6$$^{3-}$]/dt) mol l^{-1} min^{-1}.

TABLE III.[a] Effect of acetate ion on rate constant.

[CH$_3$COO$^-$] mol l^{-1}	k$_3$' (calc) mol^{-2} l^2 min^{-1}	Mean k$_3$' (obs) mol^{-2} l^2 min^{-1}
0.033	84	85
0.120	206	207
0.200	318	317

[a] Experiments at 298.1° K.

Rate constants k_1 and k_2 at I = 0.016 and 298° K are 0.31 mol l^{-1} min^{-1} and 0.14 min^{-1} respectively. No activation parameters are available and k_2 presumably refers to a slow step in the overall breakdown of the triply charged ion.

Longer term studies of the kinetics were examined by measuring the sulphite formed, titrimetrically. The kinetics were confirmed by Davis[9] who also proposed a similar first step for the reaction.

Dinegar calculated the rate constant k_1 by assuming that the dissociation constant for HS$_2$O$_3$$^-$ is 0.01 mol l^{-1} whence the rate equation for the first step becomes:
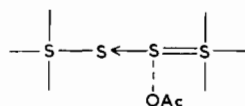
$$\text{rate} = 31[H^+][S_2O_3^{2-}]^2 \text{ mol l}^{-1} \text{ min}^{-1}$$

The third order rate constant compares favourably with a value of 38 mol^{-2} l^2 min^{-1} calculated for our uncatalysed term in the rate expression for the hexacyanoferrate(III)–thiosulphate reaction in the absence of carboxylate ion. The value is independent of ionic strength.

No deposition of sulphur is observed in our reaction. If the very early stages of thiosulphate decomposition

and of the S$_2$O$_3$$^{2-}$/Fe(CN)$_6$$^{3-}$ reaction involve the same rate determining step, hexacyanoferrate(III) must intervene to react with an intermediate, this intervention competing successfully with the normal breakdown of the intermediate.

According to Dinegar et al., the intermediate species HS$_4$O$_6$$^{3-}$ is fairly stable in aqueous solution with a half life of some 5 minutes. Agarwala et al.[10] also studied the decomposition reaction and favoured a four centred reaction with synchronous cleavage of two S–SO$_3$ bonds and formation of an S$_2$ molecule. The nature of any intermediate proposed for this work should, however, explain the general base catalysis which was identified. If S–S bonds are formed between two thiosulphate ions, they may be a result of overlap of filled $p\pi$ orbitals on one sulphur atom with empty $d\pi$ orbitals on the other; this type of bonding is frequently encountered between sulphur and oxygen atoms[12]. Thus, the electron donating atom will acquire a partial positive charge and hence anions may act to stabilise the charge:

$$-\overset{|}{\underset{|}{S}}-S\leftarrow\overset{|}{\underset{\underset{OAc}{|}}{S}}=\overset{|}{\underset{|}{S}}-$$

If this is so, then the addition of anions should also reduce the rate of decomposition of thiosulphate in acid solution.

To test this deduction we have separately studied the initial rate of production of sulphur at 298° K from thiosulphate in acid solution containing various amounts

TABLE IV. Rate of decomposition of thiosulphate in the presence of acid and acetate ions.

$10^4[H^+]$ mol l^{-1}	$10^5[S_2O_3{}^{2-}]_f{}^2$ mol^2 l^{-2}	$[CH_3COO^-]$ mol l^{-1}	$10^6 d[S]/dt$ mol l^{-1} min^{-1}	10^6 Initial Rate mol l^{-1} min^{-1} [a]
1.67	8.21	0.050	0.24	1.48
2.44	4.71	0.420	0.067	7.19

[a] Calc. rate of formation of $HS_4O_6{}^{3-}$ *via* rate = $(38 + 1400\ [CH_3COO^-])[S_2O_3{}^{2-}]_f{}^2\ [H^+]$ mol l^{-1} min^{-1}.

of acetate, using a Perkin Elmer 204 fluorescence spectrophotometer to measure scattered light at 450 nm. Consider two experiments each having $[Na_2S_2O_3]$ = 0.0102 mol l^{-1}. pH values were 3.88 and 3.77, I = 0.08 and 0.45 and the times required for appearance of colloidal sulphur were 13 and 46 minutes respectively. Taking the solubility of S atoms to be 3.1×10^{-6} mol l^{-1}, $[H^+]$ to be log^{-1} {0.505 F(I)–pH} and allowing for $NaS_2O_3^-$ formation the results are set out in Table IV.

It is clear that increase in acetate concentration does lower the rate of formation of sulphur, here even overcoming the increase in rate of formation of intermediate. In fact at high acetate ion concentration the decomposition of complex leading towards products is becoming rate-determining and the low rate of production of sulphur is consistent with stabilisation of a rather long-lived intermediate by acetate.
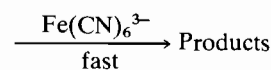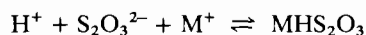
An estimation of the solvent isotope effect on the hexacyanoferrate(III)–thiosulphate reaction if reactants are $HS_2O_3^-$ and $S_2O_3{}^{2-}$ ions was made on the basis of a knowledge of ΔpK for the relevant acids in going from H_2O to D_2O, and by estimating the relative activities of various ions in the two solvents[13]. The result suggests a maximum value of 1.5 for k_{H_2O}/k_{D_2O}. The experimentally found solvent isotope effect of 1.4 is consistent with this prediction.

The Cation Catalysed Reaction

The rate law for the reaction involving cations as catalysts suggests a somewhat different process from that postulated above. The mechanism must, as in the previous case, be a spontaneous change which thiosulphate can undergo, since hexacyanoferrate(III) is not present in the rate equation. The reaction is of first order with respect to hydrogen ions, thiosulphate ions and cations. Although there are similarities in the kinetics to those reported for the exchange of oxygen between thiosulphate and water[11], there is a difference of some 19 kJ mol^{-1} between activation energies for the two processes.
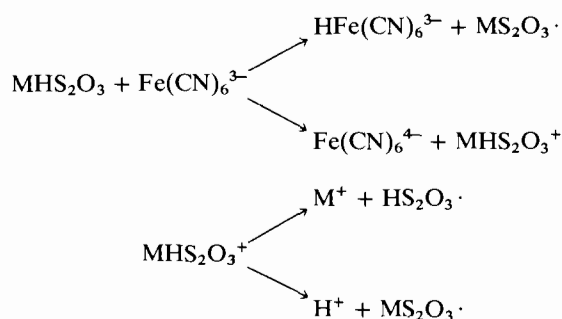
The activated complex is expected to have the composition MHS_2O_3. If mutual repulsion is the cause of the inability of $S_2O_3{}^{2-}$ and $Fe(CN)_6{}^{3-}$ to come sufficiently close for electron transfer, the ion pairing of one or other reactant with cations should assist such an encounter.

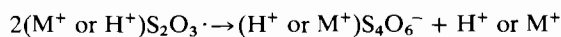The rate expression suggests the following mechanism:

$$H^+ + S_2O_3{}^{2-} + M^+ \rightleftharpoons MHS_2O_3$$

$$\xrightarrow[\text{fast}]{Fe(CN)_6{}^{3-}} Products$$

The equilibrium concentration of MHS_2O_3 is estimated to be of the order of 10^{-6} mol l^{-1} and ion pairing equilibria of this type are usually set up rapidly. The rate of a subsequent normal bimolecular process, when the concentrations of reactants are of the order of 10^{-6} and 10^{-4} mol l^{-1} with a small activation energy, will be high, and thus the low concentration of the intermediate cannot be held to account for the low rate of reaction. Further, under such conditions, it is likely that attack by $Fe(CN)_6{}^{3-}$ would become rate determining. Moreover, the experimental activation energy is 75 kJ mol^{-1} whereas addition of M^+ and H^+ would be expected to involve only some 0 to 30 kJ mol^{-1}. Presumably further energy is required to render the intermediate specialised in some way. An example of such a change could involve attack by water or some base in solution on the complex, the slow step then being, for example, the formation of a bond to sulphur, which will require activation energy.

Oxidation of the new activated complex will be fast:

$$MHS_2O_3 + Fe(CN)_6{}^{3-} \Big\langle \begin{array}{l} HFe(CN)_6{}^{3-} + MS_2O_3 \cdot \\ Fe(CN)_6{}^{4-} + MHS_2O_3{}^+ \end{array}$$

$$MHS_2O_3{}^+ \Big\langle \begin{array}{l} M^+ + HS_2O_3 \cdot \\ H^+ + MS_2O_3 \cdot \end{array}$$

followed by dimerisation of the free radicals:

$$2(M^+ \text{ or } H^+)S_2O_3 \cdot \rightarrow (H^+ \text{ or } M^+)S_4O_6^- + H^+ \text{ or } M^+$$

Previous investigators have proposed tetrathionate ion to be the major product of the initial reaction step.

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